

Electronic and Bonding Properties of Half-metallic PtMnSb and NiMnSb : First Principles Study

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(Received on : June 26, 2012)

ABSTRACT

The first principles spin-polarized self-consistent calculations of the electronic structure and charge density (CD) were performed for PtMnSb and NiMnSb to study their bonding properties. The Crystal-Orbital-Hamiltonian population (COHP) was calculated for the various bonds of these two compounds. From the CD and the COHP, the degree of hybridization was studied. The CD for PtMnSb shows a well pronounced covalent bond between Pt and Sb atoms and this is due to the strong spin-orbit coupling of PtMnSb and also this corroborates with the strong COHP peaks of Pt-Sb bonding interaction compared to that of NiMnSb. For the NiMnSb, there is no such bond. The pronounced covalent bond in PtMnSb shows the strong hybridization.

Keywords: Density functional theory; electronic band structure; charge density; chemical bonding; spin-orbit interaction.

1. INTRODUCTION

The half-Heusler intermetallic compounds are half-metallic magnets (ATX type, A= Pt, Pd, Ni, Co, Cu, Au, T=transition metal, X = metal or metalloid) with $C1_b$ structure. This structure is cubic, with A at 0,0,0; Mn at 0.25,0.25,0.25; and Sb at 0.75,0.75,0.75. Their main property is the vanishing downspin density at E_F . Among the half-Heusler half metals, the materials

namely, NiMnSb and PtMnSb belong to an interesting class of magnetic materials. These are strong ferromagnets with high Curie temperature¹. Kang *et al.*² investigated electronic structures of these compounds systematically by photoemission spectroscopy and by self-consistent spin polarized band structure calculations. The electronic structures of NiMnSb and PtMnSb have been extensively studied earlier^{5,14} by different theoretical methods.

According to the experimental investigation of the optical properties of NiMnSb thin film, the band gap is 1.1 eV^{3,21}. The magneto-optical Kerr effect for PtMnSb was first studied experimentally by van Engen *et al.*¹ and it is found to have the large Kerr effect. The electronic band structures of PtMnSb were calculated using the self-consistent Augmented Spherical Wave (ASW) method^{6,15}. Several theoretical studies^{6,11,12,14} have been carried out to explain the reason for large MOKE in PtMnSb and no specific reason has been inferred from these studies. These studies speculate the reason for the large Kerr effect in PtMnSb as due to the combined effect of the large off-diagonal dielectric tensor, spin-orbit coupling, exchange splitting, refractive index and large plasma resonance. Though the PtMnSb, NiMnSb and PdMnSb have the same magnetic moments, PtMnSb shows larger Kerr effect than the other two. Though there several studies of the above said type, to our knowledge, there are a very few reports on the chemical bonding and the Crystal-Orbital-Hamiltonian population (COHP) calculations for PtMnSb and NiMnSb.

In the present study, the self-consistent spin-polarized band structure calculations were performed on PtMnSb and NiMnSb compounds using the TB-LMTO method and the full-potential linearized augmented plane-wave (FP-LAPW) method as implemented in WIEN2K code. The charge density, chemical bonding and the Crystal-Orbital-Hamiltonian population (COHP) for PtMnSb have been calculated. From the charge density (CD) plots and the COHP profiles, the degree of hybridization was studied.

2. METHODOLOGY

Calculations have been performed using the TB-LMTO method^{7,8}, within Atomic Sphere Approximation (ASA). The calculations are scalar relativistic in nature and performed within the framework of local density approximation (LDA)¹⁷. The von Barth and Hedin⁹ exchange-correlation potential is used. Within the spheres, around each atomic center the wave function is expanded in muffin-tin orbitals. The basis set includes s,p,d orbitals at Ni, Mn And Sb atomic sites and s,p,d and f orbitals at Pt atomic site. The one-electron self-consistent potentials have been obtained by performing iterations on a grid of 512 points in the entire Brillouin zone. The tetrahedron method has been used to calculate electron density of states. In the present calculations, the accuracy in the energy convergence is 10^{-5} Ry. The experimental lattice parameters² were used to calculate the equilibrium lattice parameters. The scalar relativistic and spin-polarised calculations were performed at the calculated lattice constants to study the properties of these materials. An empty sphere with zero nuclear charge has been inserted per unit cell in the vacant site of FCC sublattice site in the C1_b structure to reduce the overlap between the adjacent atomic spheres.

The charge density of PtMnSb and NiMnSb were plotted using full-potential linearised augmented plane-wave method (FP-LAPW) within density-functional theory using WIEN2K code^{17,18}. The energy difference between the core and the valence states was set at -6 Ry. For the number of plane waves, the criterion used was that muffin-tin radius multiplied by K_{\max} (for the

plane waves) yields a value of 7.0. For the exchange and correlation functional, GGA of Perdew-Burke-Ernzerhof was used. All the calculations were performed with 1000 k points in the irreducible Brillouin zone (BZ). Both energy and charge convergence was set as the criterion for the spin-polarized self-consistent field calculations. The self-consistency was 10^{-4} e/au³ for the charge density and spin density, and the energy convergence was 10^{-5} Ry per formula unit.

3. RESULTS AND DISCUSSION

3.1. Electronic properties

The calculated spin-polarized band structures of PtMnSb and NiMnSb (not shown) in the spin up (majority spin direction) and spin down (minority spin direction) directions are given in Fig.1. The total density of states (TDOS) and atom projected density of states were calculated and are not shown here.

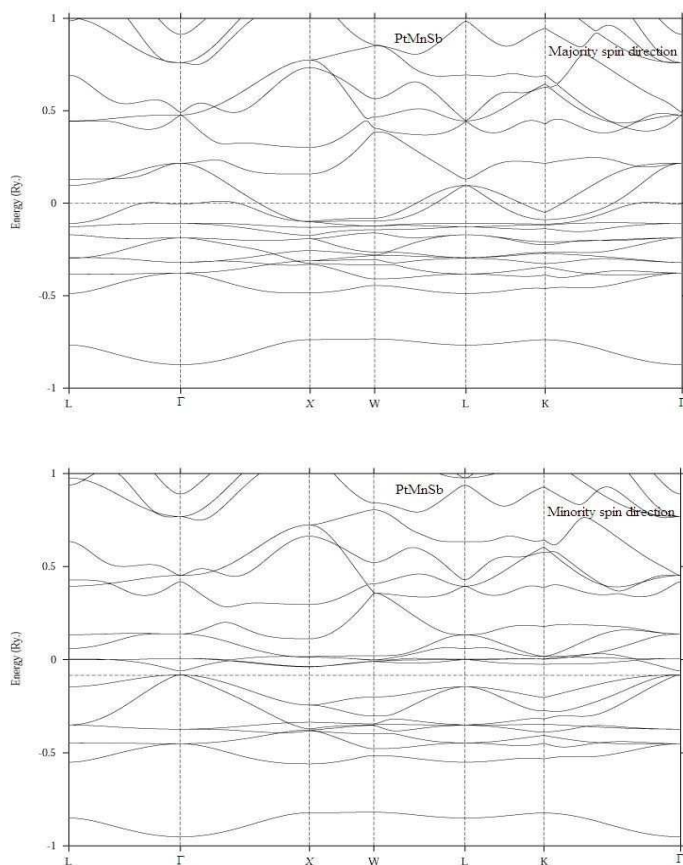


Fig.1. The calculated band structures of ferromagnetic PtMnSb in the majority and minority spin directions

The overall profiles of the band structures and DOS are the same for these three compounds AMnSb (A = Ni and Pt) in the minority and majority spin. In both the spin density, the lowest bands are Sb-s band and the bands above this are that of Sb-p, which overlap with A-s, A-p and A-d bands. In the majority spin direction, Mn-s,p and d bands overlap with A-s, p and d bands i.e., Mn and A bands are close (Fig. 1). The DOS shows that in both the spin directions, the d bands of A atoms lie below E_F which means that the d bands of A atom are occupied in both the spin directions. From the DOS, we infer that the Mn-d bands lie below E_F in the majority spin direction i.e., Mn-d bands are occupied whereas in the minority spin direction, Mn-d bands are above Fermi energy level E_F i.e., Mn-d bands are unoccupied. This is due to the strong exchange splitting of the Mn-d bands in the minority spin direction. Similar feature is observed in other ferromagnetic half-Heusler alloys also¹⁰. This splitting is responsible for the spin energy gap in these compounds in the minority spin direction. The valence bands mainly correspond to A-d like bands and Sb-p bands. The conduction bands are mainly like Mn-d bands. In the minority spin direction, from the calculated band structure and TDOS, it is seen that the Fermi energy level E_F is closer to the conduction band for Ni compound and it is closer to the valence band for the Pd and Pt compounds. The TDOS at E_F ($N(E_F)$) is given in Table 1 and these values that both PtMnSb and NiMnSb have 100% spin polarization.

3.2. Charge density and Chemical bonding

The charge density (CD) of AMnSb (A=Pt, Ni) were plotted in the majority spin

and minority spin directions using the full-potential linearised augmented plane-wave (FP-LAPW) method and are presented in Fig.2(a) to Fig.2(d). Here we concentrate on the CD plots for the minority spin direction as this gives the information about the energy gap for the spin polarization at E_F .

For PtMnSb, 2(b) show a highly directional covalent bond character between Pt and Sb atoms in both the spin directions, whereas for NiMnSb, there is no covalent bonding character between Ni and Sb as seen from Fig.2(d). In both compounds, there is no covalent bond character between A and Mn and also between Mn and Sb atoms. These A-Mn and Mn-Sb bonds are ionic in character as seen by the spherical charge distribution of these atoms without charge distribution between the atoms. It is to be noted that the ionic character is the indication of less hybridization and this also corroborates with the corresponding COHP profiles of these bonds. The COHP profiles of Pt-Sb bond and the TDOS for PtMnSb mirror the Pt-Sb covalent bond.

From the CD in the minority spin direction, one can see a layered structure and this layer consists of A, Mn and Sb atoms. These layers are well localized from each other in both the compounds. In the majority spin, these layers are delocalized and we can see the bonding between the two such layers indicating the metallic behavior in this spin direction. This bonding between the layers is stronger in NiMnSb than in PtMnSb as seen from the CD plots. This trend also agrees with the ICOHP values of the Mn-Sb bond of these two compounds as the ICOHP value of Mn-Sb bond for NiMnSb is larger than that of PtMnSb (Table 1).

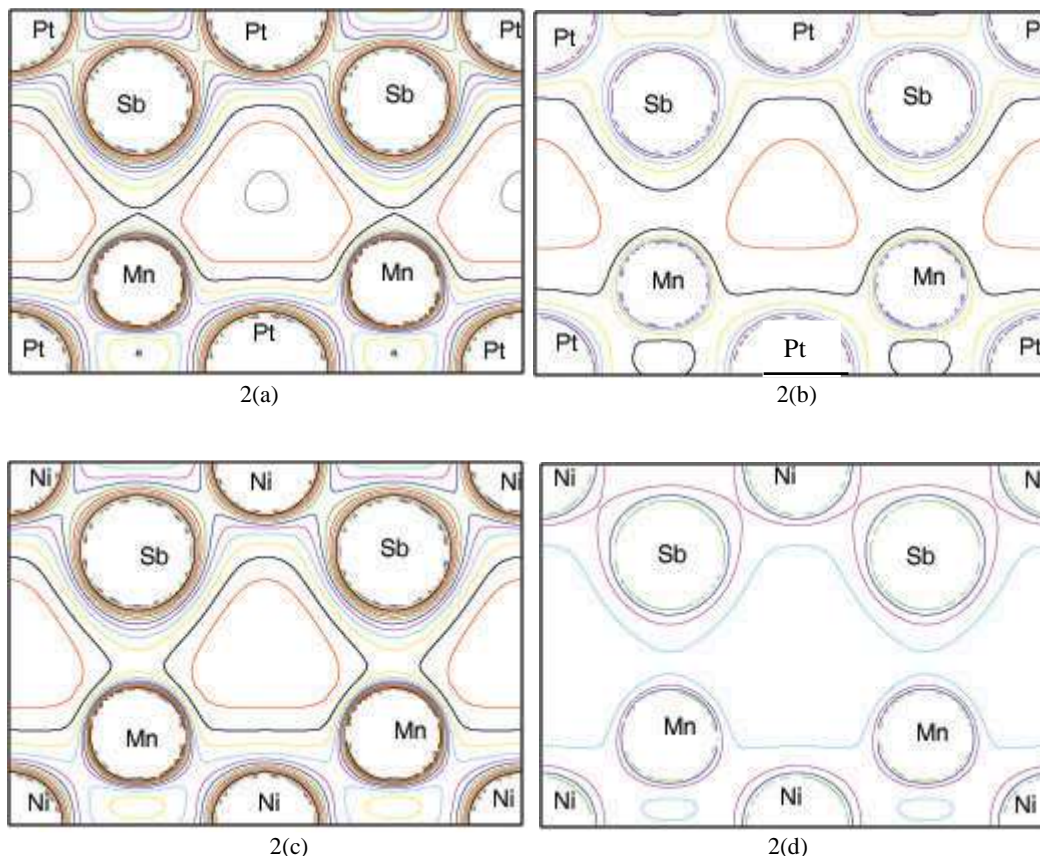


Fig. 2. Contours of charge density in the (110) plane for (a) PtMnSb in the majority spin direction (b) in the minority spin direction (c) NiMnSb in the majority spin direction (d) in the minority spin direction

3.3. Crystal -Orbital-Hamiltonian population

The Crystal-Orbital-Hamiltonian population (COHP) is the Hamiltonian-population-weighted density – of- states. It is a partitioning scheme for the band structure energy in terms of orbital-pair contributions^{19,20}. Negative values for the COHP parameter indicate bonding and the positive values indicate antibonding behavior. Thus the COHP gives energy-resolved visualization of the chemical

bonding. The bond strength between the two interacting atoms in a solid can be investigated by looking at the complete COHP between them, taking into account all valence orbitals. The integrated COHP (ICOHP) is used as a qualitative measure of mainly covalent bond strength. Table 1 gives the bond length in Å and ICOHP at E_F for PtMnSb and NiMnSb.

For the two compounds AMnSb (A=Pt, Ni), the bond strength between the pairs of interacting A, Mn and Sb atoms

were investigated by calculating the COHP. The COHP profiles for PtMnSb and NiMnSb are shown in Fig 3(a) and 3(b) respectively. For both the compounds, the s-orbital interaction predominates below -

0.4Ry. First the COHP profile for PtMnSb will be discussed and then the same will be discussed for NiMnSb. The differences between the COHP profiles for the various bonding interaction will be discussed later.

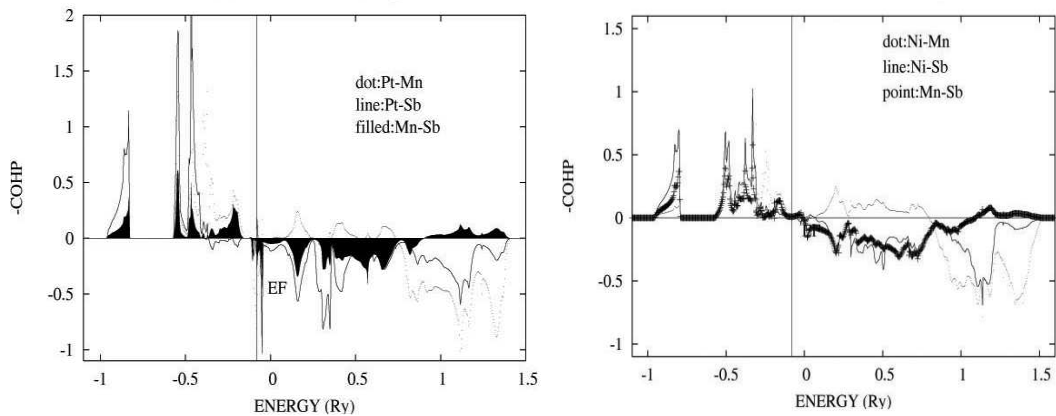


Fig. 3. (a) COHP profiles of Pt-Mn, Pt-Sb and Mn-Sb bonds of PtMnSb and (b) COHP profiles of Ni-Mn, Ni-Sb and Mn-Sb bonds of NiMnSb

The COHP profile for PtMnSb shows that the Pt-Sb bonding interactions dominate in the energy range from -1Ry to -0.85Ry and from -0.6Ry to 0.4Ry. There are two strong COHP peaks at -0.6Ry and -0.4Ry for the Pt-Sb bond interactions which corroborates with the well pronounced covalent bond between the Pt and Sb atoms. This is a special feature of PtMnSb observed

from the COHP profile of Pt-Sb indicating the large degree hybridization between Pt and Sb atoms. The peak at 0.35Ry corresponds to Pt-Mn bonding interaction and this is much smaller than that of Pt-Sb and this indicates that the Pt-Mn bonding interaction is much weaker than that of Pt-Sb bond suggesting that there is no covalent Pt-Mn bonding interaction.

Table 1 Bond length in Å°, ICOHP at E_F and TDOS at E_F (N (E_F)) in States/Ry Cell

Compound	Bond length in Å°			ICOHP at E _F			N (E _F)	↓ N (E _F) ↑
	A-Mn	A-Sb	Mn-Sb	A-Mn	A-Sb	Mn-Sb		
PtMnSb	2.686	2.686	3.102	0.139	0.146	0.057	0.00	9.7
NiMnSb	2.557	2.557	2.952	0.092	0.130	0.074	0.00	12.47

For NiMnSb, the COHP profile shows that the Ni-Sb bonding interactions are in the energy range from -1 Ry to -0.85Ry and from -0.5Ry to -0.25Ry. The corresponding peaks are much weaker than that of Pt-Sb interaction which corroborates with the absence of covalent bond between Ni and Sb atoms. This also suggests that the degree of Ni-Sb hybridization is much lower than that of Pt-Sb hybridization. The COHP peak for Ni-Mn appears at -0.2Ry which is slightly weaker than that of Ni-Sb bond. For both the compounds, the Mn-Sb COHP profiles are similar indicating same Mn-Sb bonding interactions for these compounds. Mn-Sb interactions are low and spread in the entire energy range for both compounds.

4. CONCLUSIONS

Spin polarized electronic band structure calculations were performed for PtMnSb, NiMnSb and PdMnSb using TB-LMTO and FP-LAPW methods to study the bonding properties of these compounds. The COHP was calculated for PtMnSb and NiMnSb to under the bonding interactions and hence the spin-orbit interaction of these compounds. Through these studies, we arrive at the following conclusions. The CD for PtMnSb shows a well pronounced covalent bond between Pt and Sb atoms and this is due to the strong spin-orbit coupling of PtMnSb and also this corroborates with the strong COHP peaks of Pt-Sb bonding interaction compared to that of NiMnSb. For the NiMnSb, there is no such bond. The pronounced covalent bond in PtMnSb shows the strong hybridization in PtMnSb compared to NiMnSb,

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